

Sol–gel coatings with lime repellent properties

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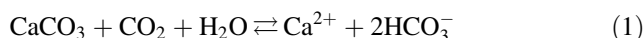
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Abstract Calcification of surfaces by hard water represents a major issue for sanitary installations. Calcium carbonate precipitates forming crusts of lime that are difficult to remove. Much effort has been undertaken to avoid scaling, most methods require chemicals or create waste. We constructed a test rig which allows for the controlled calcification of various substrates. It is found that all solid surfaces investigated calcify more or less evenly. On the other hand, surface bound poly(ethylene glycol), PEG, is known to prevent the non-specific adsorption of biomolecules. PEG coated surfaces find their use in a variety of applications. Here we show that glass and plastics, such as polyethylene, polypropylene and acrylonitrile–butadiene–styrene, can be efficiently made lime repellent by the use of sol–gel coatings containing a PEG bearing silane. It is shown that the amount of scaling is drastically reduced. Prior to coating, plastics have to be pretreated by oxygen plasma and an adhesion promoter has to be employed.

Keywords Poly(ethylene glycol) · Lime-repellent · Sol–gel coatings · Calcification · Plastic coating

1 Introduction

Calcification, or scaling, is a common nuisance. Calcium carbonate precipitates and adheres to surfaces, forming crusts of lime that are difficult to remove. Scaling of surfaces is a problem, e.g., for sanitary installations such as valves in toilet tanks, because lime may deteriorate their performance and eventually render them unusable. Calcification is dominant in areas where hard water occurs. Water hardness is brought about by dissolved alkaline earth metal ions, such as calcium and, to a lesser extent, magnesium. Hard water is found in regions rich in limestone [1], and originates from the dissolution of lime, CaCO_3 , or dolomite, $\text{CaMg}(\text{CO}_3)_2$ [2]. Reaction (1) displays this dissolution process. It is known that carbon dioxide reacts in an equilibrium process with water, forming carbonic acid. Carbonic acid reacts with CaCO_3 yielding calcium ions and hydrogen carbonate ions.



Calcium hydrogen carbonate $\text{Ca}(\text{HCO}_3)_2$ is only stable in solution. However, it displays a good solubility in contrast to the sparingly soluble CaCO_3 [3]. Scaling is the reverse reaction of the dissolution of lime (Eq. 1).

Calcification is prevented by water softening. This can be accomplished by ion exchange; alkaline earth ions are substituted by sodium ions. Dish washers, for example, use this principle to spare their heating elements. Furthermore, stains on dishes are thus avoided [4]. Detergents rely on another principle, in which complexing agents react with the calcium ions [5]. The so formed complexes strongly bind the calcium ions so that they are no longer available for scale formation. To this end, polyphosphates were often employed, but are abandoned because they lead to over-fertilization of waters. Modern detergents rather use

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zeolithes as additives, which exchange calcium for sodium ions.

An interesting approach to avoid scaling is to inhibit the adhesion of lime. This option is quite appealing as it does not consume chemicals nor creates waste. Our objective therefore is to develop a coating which prevents the adhesion of calcium carbonate crystals. It appears to us that a viable approach could be the development of hydrophilic and liquid like coatings. A promising candidate to obtain hydrophilic coatings is poly(ethylene glycol), PEG.

Reduction of protein adsorption by coating surfaces with PEG is well documented [6]. Surfaces containing PEG are interesting materials because they exhibit low degrees of protein adsorption and cell adhesion [7]. Suppression of the non-specific adsorption of biomolecules to artificial material surfaces is an important issue in the design of medical instruments [8]. Non-fouling surfaces are particularly important in, for example, blood-contacting medical devices [9], contact lenses [10] and as a non-interactive background for bio-diagnostic surfaces [11]. Incorporation of PEG to surfaces has been a proven approach in constructing bio compatible artificial implants [12]. The reasons for the ability of PEG coatings to prevent protein adsorption have been intensively discussed. However, there is no broad agreement on the molecular mechanisms underlying the protein repellency achieved with PEG coatings. This paper discusses the use of PEG coatings as lime repellent surfaces for glass and plastic materials.

2 Experimental

2.1 Instrumentation

SEM was performed with a ZEISS Supra 40VP equipped with a BRUKER, XFlash 123 eV detector for energy dispersive X-ray spectroscopy.

ATR-IR spectra were recorded on a Perkin Elmer Spectrum 100 Series spectrometer.

Contact angles were measured with a Drop Shape Analysis System from KRÜSS GmbH (Germany), model DSA10-Mk2.

2.2 Materials

The PEG-silane 2-[Methoxy(polyethyleneoxy)propyl]trimethoxysilane 90% (**1**) was purchased from ABCR (article number: AB111226). A similar product, which was also employed successfully, is Dynasylan® 4144 from Evonik Degussa GmbH. GPTMS (3-Glycidyloxypropyl)trimethoxysilane $\geq 97\%$ (**2**) was purchased from Sigma–Aldrich. Isopropanol was of purum quality. All plastic samples were of the size $50 \times 30 \times 2$ mm. Polyethylene was a high

density Borstar ME3440 type from Borealis, with carbon black as filler material. Acrylonitrile butadiene styrene, ABS, was Terluran GP35 from BASF. Polypropylene was BC245E from Borealis.

2.3 Pretreatment of the samples

Polyethylene, Polypropylene and ABS samples are cleaned with ethanol. Then they are treated with an oxygen-plasma at 0.2 mbar for 5 min. (Equipment: Femto (Diener Electronic), settings: power: 9.90; timer: 5.00; oxygen flow: 8–10). The treated samples are dip-coated within about 10 min.

Glass samples are immersed in a 2:1 mixture of 20% NaOH/30% H_2O_2 for 2 h, then rinsed with deionized water and dried.

2.4 Preparation of the sol and coating

Four mL PEG-silane (**1**) in a 25 mL 1-neck flask are dissolved in 6 mL of isopropanol, 1.7 mL of GPTMS (**2**) are added (for the glass samples GPTMS (**2**) is omitted), and then 1.25 mL of 0.01 M hydrochloric acid are added. The flask is stoppered with a septum and the solution is stirred for 18–22 h. The resulting sol is diluted with isopropanol to 100 mL in a beaker. Pretreated samples are immersed in the above solution for a few minutes, then slowly withdrawn and air-dried for about 30 min. Thereafter, the plastic samples are cured at 90 °C for about 5 h. The glass samples are cured at 120 °C for about 1 h.

3 Results and discussion

In order to study the calcification of different substrates, a test rig which allows controlled and reproducible calcium carbonate deposition is constructed. A top view of the test rig is shown schematically in Fig. 1. Six liters of a solution which is 10 mM in NaHCO_3 and 5 mM in CaCl_2 is

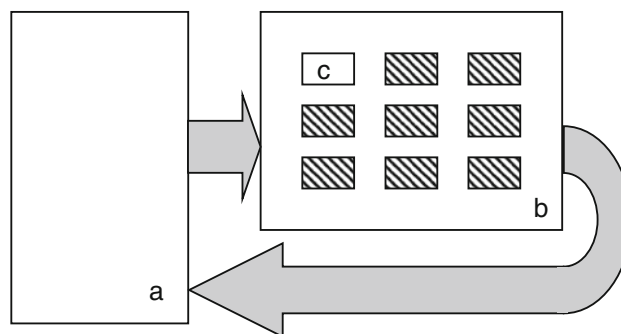


Fig. 1 Top view of the calcification test rig. **a** Hard water storage vessel and thermostat. **b** Test block with cavities for nine samples. **c** Sample

employed as source of the CaCO_3 . This solution is prepared in the storage vessel (a) which is kept at a constant temperature of 20 °C. The solution is pumped through the test block (b) where 9 samples (c) await calcification. The samples are submerged in a laminar flow of the solution during exposure. Standard calcification is carried out for 16 h. Thereafter, the samples are dipped in deionized water to remove weakly adhering CaCO_3 and then dried. The resulting surface scaling is investigated by light microscopy and scanning electron microscopy (SEM), for an example see Fig. 2. The samples are weighted before and after calcification, and the amount of adhering CaCO_3 is thus determined. However, it is often possible to optically observe the degree of calcification.

Since little is known about how lime binds to a material, we have investigated various uncoated substrates with respect to their ability to repel calcification. Table 1 summarizes the results. The samples in Table 1 are not coated. The materials are calcified in the test rig for 16 h, after which the amount of CaCO_3 sticking to the sample is

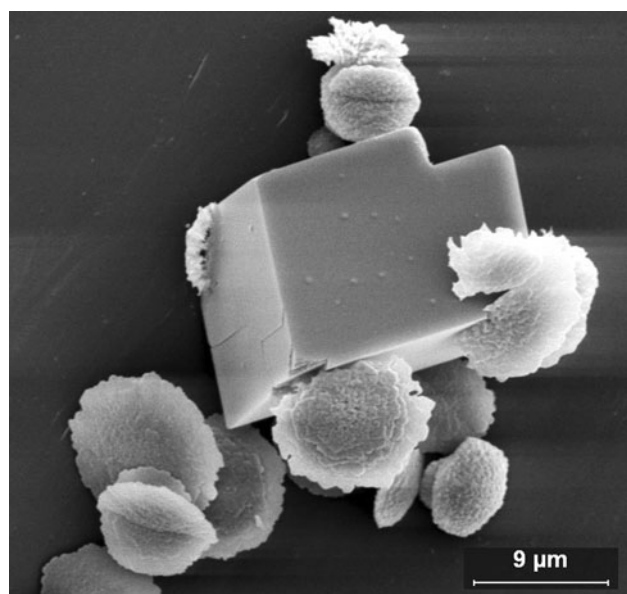


Fig. 2 A SEM picture of calcium carbonate crystals on a polyethylene surface. *Cube* Calcite, *discs* Vaterite

determined. For each run an internal standard (ABS, acrylonitrile butadiene styrene) is also investigated. The amount of CaCO_3 on the sample is compared to the amount of CaCO_3 on the reference. It is seen that the ABS reference always calcifies slightly more than the other materials. The main result, however, is that all solid materials investigated are calcified more or less uniformly. Glass, polar (ABS), and even non-polar plastics such as PE (poly(ethylene)); PP (poly(propylene)); SB (styrene-butadiene) and PVDF (poly(vinylidene fluoride)) are calcified equally. One concludes that hydrophobicity therefore does not hinder calcification.

We did not find a solid material which is not prone to calcification. As a consequence we investigated PEG containing coatings, as PEG forms liquid-like films in contact with water to which calcium carbonate crystals might not adhere. We decided to investigate coatings based on sol-gel techniques [13]. Figure 3 shows the PEG-silane (**1**) that is used as precursor. A methyl terminated PEG chain is bound to a silicon atom bearing three hydrolysable groups. Compound **1** consists of a mixture of molecules having different chain lengths; the PEG chain contains mainly 6–9 repeating ethylene oxide units. After usual sol-gel reactions, one half of a clean glass substrate is coated with the sol by dipping and cured. Figure 4 displays the glass plate after calcification. It is seen, that the uncoated side (Fig. 4, to the right) is

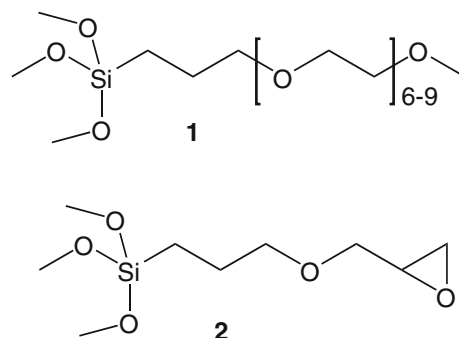


Fig. 3 PEG-silane (**1**). Compound **1** is a mixture of molecules with different poly(ethylene glycol) chain length, 6–9 repeating units are prevailing. (3-Glycidyloxypropyl)trimethoxysilane, GPTMS (**2**) is an adhesion promoter and crosslinker

Table 1 Calcification of different materials

	Material	Number of samples	Amount of CaCO_3 after 16 h (mg)	CaCO_3 on internal reference (ABS) (mg)	Amount of CaCO_3 relative to reference
1	ABS	9	20.6 ± 1.3		
2	PE-HD	3	10.4 ± 0.5	11.3 ± 0.2	0.92 ± 0.05
3	PP	3	12.2 ± 0.8	13.9 ± 0.7	0.88 ± 0.07
4	SB	3	8.8 ± 0.1	10.5 ± 0.7	0.84 ± 0.01
5	PVDF	2	13.3	13.7	0.97
6	Glass	6	10.9 ± 1.4	12.9 ± 2.6	0.85 ± 0.11

The substrates are not coated. The amount of calcium carbonate deposited on the sample after 16 h is compared to an internal reference

covered with lime, whereas the coated section (Fig. 4, to the left) is lime free. The amount of CaCO_3 adhering to two fully coated glass plates is displayed in Table 2, entry 4. In contrast to the uniformly calcified substrates (see Table 1) the coated glass plates are almost lime free, only fractions of CaCO_3 are found compared to the reference. The coating therefore efficiently inhibits calcification.

For many applications, plastics are more interesting substrates than glass, since, for example, sanitary installations are made thereof. Because plastics have non-reactive surfaces, sol–gel coating is difficult. Oxygen-plasma activation of the plastic sample is a method to increase the surface energy and to render it hydrophilic [14]. This activation introduces, among others, hydroxyl groups at the surface to which the silanes may bind. However, it turned out that plasma activation alone is not sufficient to attach the sol, no anti-calcification effect was achieved. We therefore searched for an adhesion promoter. It was found that by the addition of GPTMS (2) (see Fig. 3), combined with plasma activation, PE, PP and ABS could be made lime repellent. Supposedly, the GPTMS (2) acts as a bifunctional primer. The epoxide-group could react with a hydroxyl-group from the activated substrate, and the silane could be incorporated into the sol–gel network, thus crosslinking surface and coating.

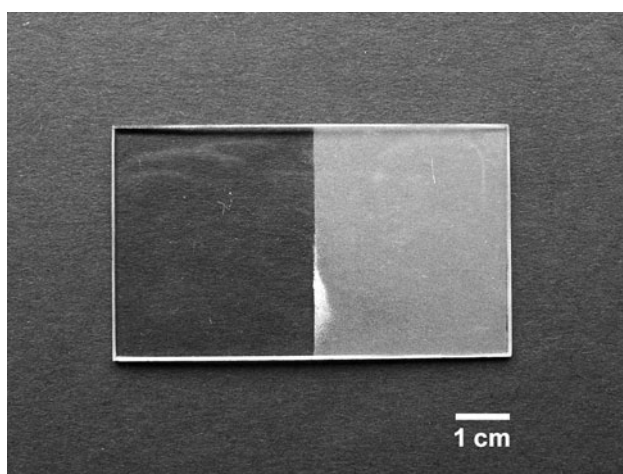


Fig. 4 A glass plate after calcification. The *left half* is coated and lime free, whereas the *right half* is uncoated and covered with lime [20]

Table 2 summarizes the results achieved with coated specimens. ABS, PE, PP and glass were coated according to the procedures given in the experimental section and then calcified, together with uncoated ABS references. The amounts of calcium carbonate found on the coated samples are compared to the internal references. It is seen that only a few percent of the calcium carbonate observed on the reference are found on the coated specimens.

In Fig. 5, a coated and calcified PE sample is displayed. Because the PE is dyed with carbon black as an additive, the white lime is well visible after calcification. Two thirds of the sample are coated and are thus lime free, whereas the not coated third is covered with calcium carbonate. Also, other plastics, such as PP and ABS, are coated in the same way. Figure 6 shows a micrograph of an ABS substrate after calcification. Again, on the coated side, much less calcium carbonate crystals are observed than on the uncoated side. This demonstrates that poly(ethylene glycol) at surfaces efficiently prevents the adhesion of calcium carbonate crystals [15].

Prior to the surface analyses the samples were rinsed with water for 1 min and then dried at room temperature. Coating thickness was investigated using scanning electron microscopy (SEM) equipped with energy dispersive X-ray spectroscopy on an aluminum substrate. The microscope

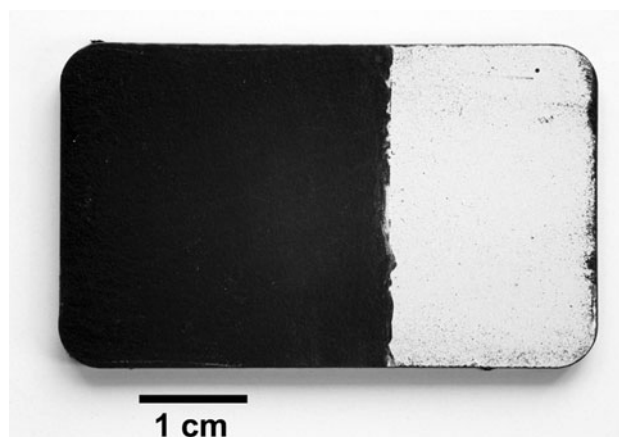


Fig. 5 A polyethylene sample after calcification. The *left two thirds* are coated and withstand calcification, whereas the *third to the right* is uncoated and therefore covered with lime. (The polyethylene sample is black because it contains carbon black as filler)

Table 2 Calcification of coated samples

Only 2.3–7.4% of calcium carbonate relative to a not coated internal reference are found on the coated specimens

	Material	Number of samples	Amount of CaCO_3 after 16 h (mg)	CaCO_3 on internal reference (ABS) (mg)	Amount of CaCO_3 relative to reference
1	ABS	2	0.30/0.97	13.12 ± 0.70	0.023/0.074
2	PE-HD	2	0.75/0.61	13.12 ± 0.70	0.057/0.046
3	PP	2	0.78/0.57	13.12 ± 0.70	0.059/0.043
4	Glass	2	0.30/0.42	13.03/13.16	0.023/0.032

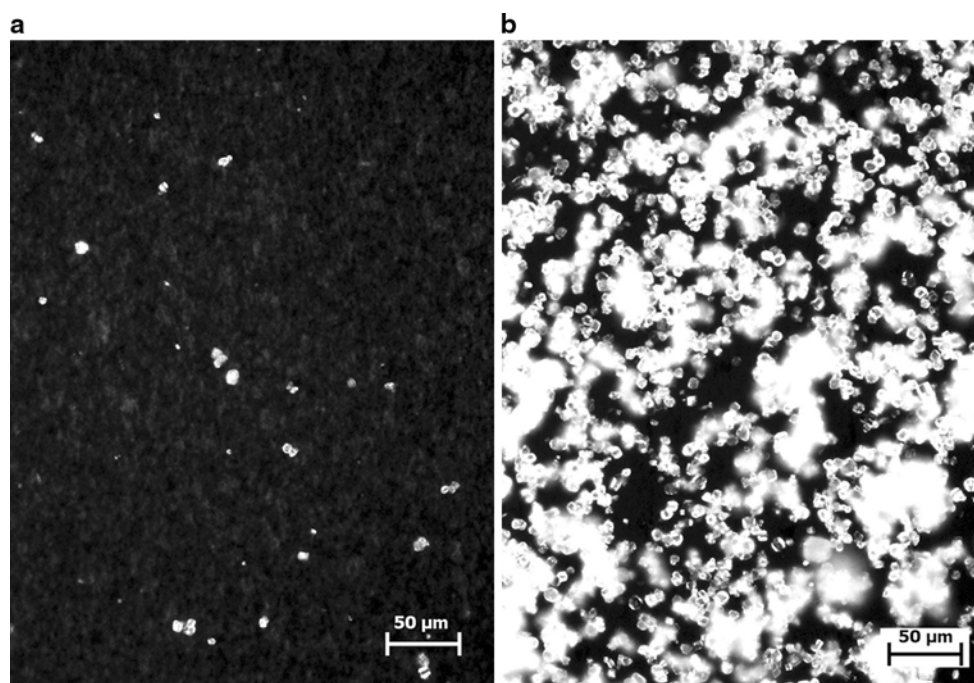


Fig. 6 Micrograph of an ABS sample after calcification. *Left* Coated side, few calcium carbonate crystals; *right* Uncoated side, many calcium carbonate crystals [20]

was focused on the coating surface. Then, the energy of the electron beam was increased stepwise until the characteristic $K\alpha$ radiation (1.4866 keV) of aluminum was observed. From the threshold energy of the electron beam yielding the aluminum $K\alpha$ radiation the coating thickness was calculated using Monte Carlo Simulation [16]. Three different spots were investigated and the mean coating thickness was determined to be 170 ± 40 nm.

Water- and diiodomethane contact angles were determined for uncoated and coated ABS, PE and PP (see Table 3). Whereas typical values for the uncoated polymer samples are obtained, the coated specimens consistently show very small ($<10^\circ$) water and diiodomethane contact angles. Hence, the coating renders the surface of the sample hydrophilic and oleophilic, as it is expected for PEG on the surface.

Attenuated Total Reflection Infrared Spectroscopy (ATR-IR) can be used for surface analysis. The penetration

depth of the infrared light into the sample is typically between 0.5 and 2 μm , with the exact value being determined by the wavelength, the angle of incidence and the indices of refraction for the ATR crystal and the medium being probed [17]. Figure 7 shows the ATR-IR spectra of uncoated and coated ABS. The spectrum above stems from uncoated ABS, whereas the spectrum below was recorded with coated ABS. It is seen that the coated sample shows a strong absorption at around $1,100\text{ cm}^{-1}$, in addition to the bands of ABS. The band at $1,100\text{ cm}^{-1}$ is attributed to the

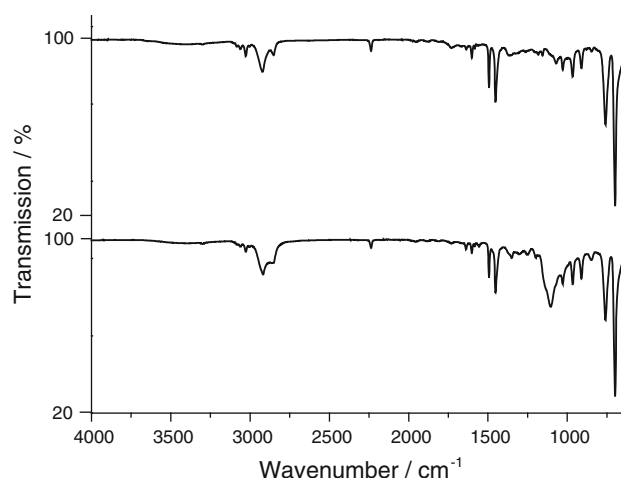


Fig. 7 Attenuated Total Reflection Infrared Spectra (ATR-IR) of coated (*bottom*) and uncoated (*top*) ABS. Siegmann and Hirayama

Table 3 Water (H_2O) and diiodomethane (CH_2I_2) contact angles for coated and uncoated polymer samples

	Contact angle (H_2O) ($^\circ$)		Contact angle (CH_2I_2) ($^\circ$)	
	Uncoated	Coated	Uncoated	Coated
PE	96 ± 2	<10	49 ± 1	<10
PP	82 ± 2	<10	45 ± 5	<10
ABS	74 ± 4	<10	27 ± 3	<10

asymmetric stretch vibration of the C–O–C moieties of the PEG molecule [18]. Also, the asymmetric stretch vibration of the Si–O–Si groups of the sol–gel network lies approximately at that wavenumber [19]. The ATR-IR spectra of coated PP and PE also show absorption at around $1,100\text{ cm}^{-1}$.

It is concluded that the observed IR absorption at around $1,100\text{ cm}^{-1}$ is consistent with a sol–gel coating containing PEG.

4 Conclusion

The precipitation of calcium carbonate to sanitary installations exposed to hard water causes costly repair. In order to prevent calcification we examine the behavior of various materials. A test rig for the investigation of calcification was constructed. It is found that all uncoated solid substrates examined calcify more or less the same. Since poly(ethylene glycol) at surfaces is known to inhibit bio-fouling and is forming liquid-like surfaces, sol–gel coatings containing poly(ethylene glycol) are investigated for their ability to avert calcification. Glass and polymer surfaces such as polyethylene, polypropylene and acrylonitrile–butadiene–styrene can be coated using a poly(ethylene glycol) bearing silane. The polymer substrates have to be pretreated by oxygen plasma and an adhesion promoter has to be employed. We demonstrate that those PEGylated surfaces efficiently inhibit calcification.

The coated polymer samples were analyzed by scanning electron microscopy (SEM), contact angle measurement and attenuated total reflection infrared spectroscopy (ATR-IR). SEM was used to determine coating thickness, which was found to be $170 \pm 40\text{ nm}$. Contact angles were found to be very low, both for water and diiodomethane, which is consistent with poly(ethylene glycol) at the surface. In addition to the bands of the polymer, the ATR-IR spectra of the coated substrates revealed an absorption at around $1,100\text{ cm}^{-1}$ which is attributed to the asymmetric

stretch vibration of the C–O–C and Si–O–Si moieties of poly(ethylene glycol) and the sol–gel network, respectively.

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References

1. Kölle W (2003) Wasseranalysen—richtig beurteilt. 2. Auflage. Wiley-VCH, Weinheim
2. Morse JW, Arvidson RS (2002) *Earth-Sci Rev* 58:51–84
3. Plummer LN, Busenberg E (1982) *Geochim Cosmochim Acta* 46:1011–1040
4. Dia MA, Lo SM, Pontie M, Bagan H, Diawara CK, Rurneau M (2006) *C R Chim* 9:1260–1267
5. Smulders E (2002) *Laundry detergents*. Wiley-VCH, Weinheim
6. Harris JM, Zalipsky S (eds) (1997) *Poly(ethylene glycol) chemistry and biological applications*. ACS symposium series 680, Am Chem Soc, Washington DC
7. Kingshott P, Griesser HJ (1999) *Curr Opin Solid St M* 4:403–412
8. Tan J, Brash JL (2009) *J Biomed Mater Res A* 90A:196–204
9. Lee JH, Lee HB, Andrade JD (1995) *Prog Polym Sci* 20: 1043–1079
10. Jang HN, Chung YB, Kim SS (2009) *Polymer-Korea* 33:169–174
11. Popat KC, Johnson RW, Desai TA (2003) *J Vac Sci Technol B* 21:645–654
12. Fukai R, Dakwa PHR, Chen W (2004) *J Polym Sci Pol Chem* 42:5389–5400
13. Bötcher H (2001) *Mat-wiss u Werkstofftech* 32:759–766
14. Liston EM, Martinu L, Wertheimer MR (1993) *J Adhes Sci Technol* 7:1091–1127
15. Hirayama M, Meier L (2007) *Europ Pat EP 1 816 155 A1*
16. Joy DC (1995) *Monte Carlo modeling for electron microscopy and microanalysis*. Oxford University Press, New York
17. Mirabella FM Jr (1993) In: Mirabella FM Jr (ed) *Practical spectroscopy series; internal reflection spectroscopy: theory and applications*. Marcel Dekker, Inc, New York
18. Pretsch E, Bühlmann P, Affolter C, Badertscher M (2001) *Spektroskopische Daten zur Strukturaufklärung organischer Verbindungen*, 4. Auflage. Springer Verlag, Berlin
19. Gillespie RJ, Robinson EA (1964) *Can J Chem* 42:2496–2503
20. Siegmann K, Hirayama M (2008) *Chimia* 62:815–819